SCIENCE FOR CERAMIC PRODUCTION

SINTERING KINETICS OF HIGH-ALUMINA CERAMICS WITH COMPLEX ADDITIVES

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Results of a study of ceramic compaction kinetics under conditions of isothermal and nonisothermal heating are given. Kinetic equations of the compaction process using a structure/energy parameter as the dependent variable are given, and on this basis values of apparent activation energy for two compaction stages are determined. It is demonstrated that modification transitions and formation of unstable phases and solid solutions in the course of ceramic firing have a substantial effect on the mechanism of ceramic compaction.

Firing is the final stage of ceramic technology, when the condensed structure of an article is converted to a crystallized structure, which is a higher-order structure. As a consequence of the physicochemical and sintering processes that take place in firing, individual weakly bonded particles agglomerate into a dense mass with the required physicochemical properties. The fact of attaining a prescribed level of these properties is largely determined by the time/temperature conditions of the sintering process. The course of compaction of the material is usually monitored by absolute or relative values of shrinkage, density, or porosity, whose variations are used to predict the kinetic regularities of compaction of the material in sintering. For instance, in [1] monitoring of the process is implemented based on the degree of compaction:

$$C = (\rho_2 - \rho_1)/(\rho_t - \rho_1) = (K_{s_2} - K_{s_1})/1 - K_{s_1}, \qquad (1)$$

where ρ_1 and ρ_2 are the apparent density of the material before and after firing; ρ_t is the true density of the material; K_{s_1} and K_{s_1} are the solid-phase volume concentration before and after firing, in relative units.

It follows from Eq. (1) that the parameters K_{s_2} and C are interrelated by a linear dependence:

$$\begin{cases} K_{s_2} = CP_1 + K_{s_1}; \\ P_1 = 1 - K_{s_1}, \end{cases} \qquad (2)$$

where P_1 is the material porosity before firing.

The parameters K_{s_2} and C differ only in their variation limits: $0 < C \leq 1$ and $K_{s_1} \leq K_{s_2} \leq 1$, and therefore, there is no difference in principle in using them to control the degree of compaction of the material. It should be noted that the use of compaction parameters normalized to variation within the limits of $0 - 1$ produces very complicated kinetic equations, since these parameters only reflect the material compaction process and are not related to the mechanism of this process.

V. A. Ivensen [2] observed that study of the sintering process is effective in the case where the variation of the selected dependent variable reflects most completely the principal features of the material compaction mechanism. The structure/energy parameter n [3, 4], which can be determined from the relationship

$$K_{s_2}/(1 - K_{s_2}) = (nK_{s_1})/(1 - K_{s_1}) \text{ or } K_{s_2}/P_2 = (nK_{s_1})/P_1,$$

is suggested as such a variable that reflects the process of material compaction in sintering.

The purpose of the present study is to elucidate the possibilities of the parameter n in studying the kinetics of sintering of a material whose true density and phase composition change in sintering.

The ceramic mixture used in the experiments contained 70% technical alumina and 30% bauxite from the Tatarskii deposit (Krasnoyarsk Region). The chemical composition of the mixture and its components is shown in Table 1.

To produce a ceramic mixture, the initial batch was subjected to wet vibration compaction for 2 h to accomplish a dispersity with a prevailing particle size of $2 - 3$ μm. The in-

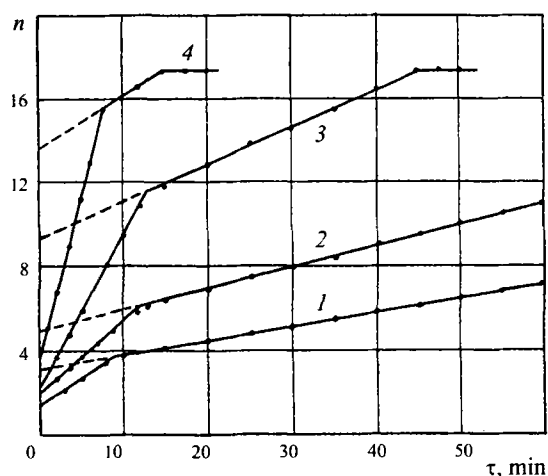[1] Tomsk Polytechnic University, Tomsk, Russia.

Fig. 1. Kinetics of material compaction in isothermal heating: *1, 2, 3,* and *4*) temperature of 1350, 1400, 1450, and 1500°C, respectively.

troduction of bauxite into the mixture composition is determined by the following factors.

First, as a mixture component bauxite acts as a plastifier, since it contains such bauxite-forming minerals as gibbsite, hydrogoethite, kaolinite, and others, which have a highly defective crystalline structure. The products of dispersion of these minerals in water impart plastic properties to the ceramic mixture that make it possible to produce small-sized articles, such as calibrated abrasive grains [5, 6], by the plastic molding method.

Second, introduction of bauxite into the mixture involves the introduction of iron, silicon, and titanium oxides, which facilitate a decrease in the temperature of corundum sintering [7]. Due to a rather high rate of diffusion of titanium ions in alumina, γ-Al_2O_3 completely recrystallizes to α-Al_2O_3 at temperatures of 1200 – 1300°C. In a reducing medium titanium oxide (Ti_2O_3) forms with Al_2O_3 an unstable interstitial solid solution capable of decomposing in an oxidizing medium. At a temperature of 1318°C aluminum and iron oxides form spinel (hercynite) and various solid solutions whose compositions are determined by the ratio between these oxides in the fired material and by the firing temperature [8]. It can be assumed that the instability of hercynite as an independent phase and solid solutions of variable composition

that are formed upon introduction of a complex additive is an important factor determining the temperature and kinetics of sintering of high-alumina ceramics.

In studying the sintering kinetics, disk-shaped samples 17 mm in diameter and 3 mm high were used, which were obtained by compression of a mixture with an absolute moisture content of 26% at a pressure of 7 MPa. The samples were dried in an alumina charge at the temperature of 150°C and then heated at a rate of 2°C/min to 650°C to remove chemically bound water. Isothermal heating of the samples was performed in a tubular furnace with platinum-rhodium wire heaters at temperatures of 1350 – 1500°C with an interval of 50°C. Before being brought to the high-temperature zone of the furnace, the samples were preheated to 1100°C.

The true density of the material in the initial state was 3518 kg/m^3, K_{s_1} = 0.58. The shrinkage of the samples in diameter was recorded using a dilatometric method with simultaneous determination of their apparent and true density values, which were used to compute the values of K_{s_2}. It was found in the experiments that there is a linear relationship between K_{s_2} and the relative shrinkage of the samples:

$$K_{s_2} = 1.565 \cdot 10^{-2} \, (\Delta D/D_0) + 0.58,$$

where $\Delta D/D_0$ is the relative linear shrinkage of the sample in diameter, %.

Using known values of K_{s_1} and K_{s_2} and Eq. (2), the parameter *n* was determined. The graphical dependences $\Delta D/D_0 = f(\tau)$ and $K_{s_1} = f(\tau)$ are of a similar nature and are typical of these processes. The dependence $n = f(\tau)$ at constant temperatures exhibits two straight segments with different angular coefficients (Fig. 1). The mathematical formulas of the dependences are given in Table 2.

In the general case the dependences $n = f(\tau)$ can be represented in the form

$$n = n_0 + k\tau,$$

where *k* is the compaction rate constant, min^{-1}.

Using known values of *k* and the graphical dependences $\ln k = f(1/T)$ in accordance with the Arrhenius equation, the apparent activation energy of ceramic compaction in sintering

TABLE 1

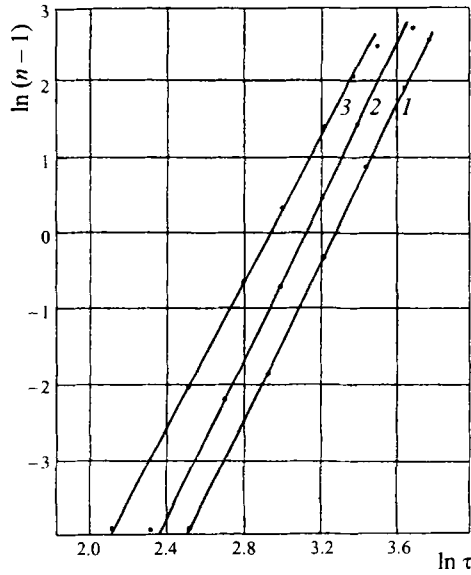| Material	Weight content, %						
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	other	calcination loss
Tatarskii bauxite	45.75	10.01	17.51	4.22	0.39	0.22	21.93
Technical alumina	98.33	0.08	0.03	–	–	0.56	1.00
Batch	82.54	3.06	5.27	1.26	0.11	0.45	7.28
Batch (converted to calcined material)	88.97	3.29	5.68	1.35	0.12	0.48	–

Fig. 2. Kinetics of material compaction in nonisothermal heating within the temperature interval of 1100 – 1500°C: *1, 2*, and *3*) heating rates of 8, 10, and 12 C/min, respectively.

was determined. It was established that the first compaction segment is characterized by two values of the activation energy: $E_1 = 140.9$ kJ/mole (1350 – 1410°C) and $E_2 = 392.1 \pm 3.95$ kJ/mole (1410 – 1500°C), and the second segment is characterized by the single value $E = 210.3$ kJ/mole (1350 – 1500°C). This behavior of the material in sintering can be accounted for by the manifestation of two elementary acts of the compaction mechanism. In the initial period ($\tau < 10$ min) at a temperature of 1350 – 1410°C, the material is mostly compacted due to the transition γ-$Al_2O_3 \rightarrow$ α-Al_2O_3, which is accompanied by a decrease in volume of 14.3% and a thermal effect of 32.76 kJ/mole, as well as formation of hercynite ($\rho_t = 3900$ kg/m^3). In the second stage of sintering ($\tau > 12$ min) at a temperature of 1350 – 1500°C the material is compacted due to recrystallizing amalgamation of fine corundum crystals and formation of a fine-crystalline block structure of the ceramic.

An increase in the temperature of isothermal heating in the initial stage (1410 – 1500°C) produces intense ceramic compaction caused by a parallel-sequential compaction procedure due to modification transitions, formation and disinte-

gration of the spinel phase and solid solutions, and recrystallizing amalgamation of fine corundum crystals. The appearance of small quantities of melt in the fired material at these temperatures also facilitates the compaction process. Therefore, the increased value of E_2 represents the aggregate energy of different elementary acts of the compaction process and determines the significant effect of temperature on the ceramic compaction rate constant.

Nonisothermal sintering of the ceramics was studied by heating samples from an initial fixed temperature of 1100°C to 1500°C at a heating rate of 8, 10, and 12°C/min. The shrinkage of samples was recorded in the same way as in isothermal heating. The dependences $\Delta D/D = f(\tau)$ and $K_{t_2} = f(\tau)$ are S-shaped curves where the beginning of shrinkage is observed at a temperature of 1150 – 1170°C. The dependence $n = f(\tau)$ is exponential and has the form

$$n = 1 + e^{K \ln \tau}/e^b,$$

which can be represented as

$$\ln(n - 1) = Kn\tau - b, \qquad (3)$$

where K is a coefficient that determines the rate of compaction of the given material, min^{-1}; b is a constant coefficient for a given heating rate.

At $\tau = 0$ $\ln(n - 1) = -b$, which is possible for the values $1 < n < 2$, and at $n = 2$, $\ln(n - 1) = 0$ and $K \ln \tau = b$. It is seen in Fig. 2 and Table 3 that the dependences $\ln(n - 1) = f(\tau)$ are virtually straight lines for all heating rates for low values of the coefficient K:

for 8°C/min, $\ln(n - 1) = 5.125 \ln \tau - 16.71$;

for 10°C/min, $\ln(n - 1) = 5.175 \ln \tau - 16.16$;

for 12°C/min, $\ln(n - 1) = 4.891 \ln \tau - 14.38$.

The closeness of the values of K points to the fact that this coefficient characterizes the compaction rate of a material of a certain type and chemical composition and cannot be used to calculate the kinetic parameters of compaction.

In order to elucidate the parameter that is the kinetic constant of the compaction rate, let us use the following method. Let $\ln(n - 1)_2$ correspond to greater compaction at a given heating rate, and $\ln(n - 1)_1$ correspond to lesser compaction. Then, according to Eq. (3)

$$\ln(n - 1)_2 + b = K \ln \tau_2; \qquad (4)$$

$$\ln(n - 1)_1 + b = K \ln \tau_1. \qquad (5)$$

By subtracting Eq. (5) from Eq. (4) we get:

$$\ln(n - 1)_2 - \ln(n - 1)_1 = K(\ln \tau_2 - \ln \tau_1).$$

TABLE 2

Firing temperature, °C	First segment, $\tau < 12$ min	Second segment, $\tau > 12$ min
1350	$n = 1.5 + 0.25\tau$	$n = 3.1 + 0.066\tau$
1400	$n = 2.0 + 0.345\tau$	$n = 4.87 + 0.102\tau$
1450	$n = 2.3 + 0.72\tau$	$n = 9.5 + 0.175\tau$
1500	$n = 3.7 + 1.52\tau$	$n = 13.6 + 0.246\tau$

TABLE 3

Heating temperature, °C	Heating rate 8°C/min					Heating rate 10°C/min					Heating rate 12°C/min				
	τ, min	$\ln\tau$	K_{s_2}	n	$\ln(n-1)$	τ, min	$\ln\tau$	K_{s_2}	n	$\ln(n-1)$	τ, min	$\ln\tau$	K_{s_2}	n	$\ln(n-1)$
1100	0	–	0.580	1.00	–	0	–	0.580	1.00	–	0	–	0.580	1.00	–
1200	12.5	2.52	0.585	1.02	–3.91	10	2.30	0.585	1.02	–3.91	8.3	2.11	0.585	1.02	–3.91
1250	18.7	2.93	0.615	1.15	–1.85	15	2.71	0.604	1.11	–2.20	12.5	2.52	0.610	1.13	–2.02
1300	25.0	3.22	0.705	1.73	–0.314	20	2.99	0.674	1.49	–0.70	16.6	2.81	0.681	1.54	–0.60
1350	31.2	3.44	0.827	3.46	0.90	25	3.22	0.780	2.56	0.449	20.8	3.03	0.769	2.42	0.35
1400	37.5	3.62	0.917	8.00	1.94	30	3.40	0.880	5.31	1.46	25.0	3.22	0.877	5.16	1.42
1450	43.7	3.77	0.951	14.00	2.57	35	3.55	0.935	10.40	2.24	21.1	3.37	0.925	8.93	2.07
1500	50.0	3.91	0.958	16.50	2.74	40	3.68	0.958	16.50	2.74	33.3	3.50	0.948	13.20	2.50

Since $\ln\tau_2 = K^1/T_2$, $\ln\tau_1 = K^1/T_1$, and $K = K_0 e^{-E/RT}$, then

$$\ln(n-1)_2 - \ln(n-1)_1 = K^1 K_0 (e^{-E/RT_2} - e^{-E/RT_2}). \quad (6)$$

By taking the logarithm of Eq. (6) we arrive at

$$\ln[\ln(n-1)_2 - \ln(n-1)_1] = -E/(RT_2) + E/(RT_1)$$
$$= E/R(1/T_1 - 1/T_2),$$

or finally

$$\ln[\ln(n-1)_2/(n-1)_1] = E/R(1/T_1 - 1/T_2). \quad (7)$$

Equation (7) can be obtained as well by dividing Eqs. (4) and (5):

$$\frac{e^{\ln(n-1)_2}e^b}{e^{\ln(n-1)_1}e^b} = \frac{K\ln\tau_2}{K\ln\tau_1} = \frac{K^1 K_0 e^{-E/RT_2}}{K^1 K_0 e^{-E/RT_1}}.$$

It follows from Eq. (7) that the quantity $n - 1$ is the compaction rate constant in ceramic sintering. The construction of the graphical dependence in the coordinates
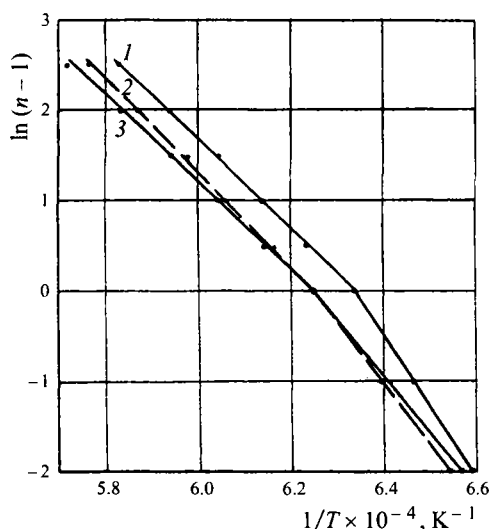

Fig. 3. Dependence of the logarithm of the compaction rate constant on the inverse temperature. Notation as in Fig. 2.

$\ln(n-1) = f(1/T)$ makes it possible to determine the apparent activation energy of the compaction process in nonisothermal heating. It is seen in Fig. 3 that the temperature dependence of $\ln(n-1)$ is represented by two straight segments with a bend point at $\ln(n-1) = 0$. The conclusion can be drawn that for the most part, two compaction mechanisms are manifested in sintering of the considered ceramics, regardless of the heating rate, and the compaction mechanism changes at $n = 2$. The values of the activation energy determined from Table 3 and Fig. 3 are shown in Table 4.

The absolute temperature of heating the material in this case was calculated from the formula

$$T = 273 + (t_i + dt/d\tau \cdot \tau),$$

where t_i is the initial temperature of the material, °C; $dt/d\tau$ is the heating rate, °C/min; τ is the heating duration, min.

The data of Table 4 give grounds for the important conclusions that the expenditure of energy on compaction of the material in nonisothermal heating is much higher in the initial stage (E_1, $n < 3$, $\ln(n-1) < 0$) than the expenditure of energy in the second phase of sintering (E_2, $n > 2$, $\ln(n-1) > 0$), whereas E_2 virtually does not depend on the heating rate. Moreover, an increase in the heating rate in the first stage of compaction facilitates a decrease in energy expenditure, but at the same time, with a lower heating rate, the material becomes more sensitive to temperature variations due to accumulation of larger imperfections both in individual particles and in the whole structure of the heated material. It follows from Fig. 3 that the compaction mechanism changes within the temperature interval of 1308 – 1324°C, i.e., at the temperature of hercynite formation and its sub-

TABLE 4

Material heating rate, °C/min	E_1, kJ/mole	E_2, kJ/mole
8	204.3	159.3
10	198.7	150.8
12	180.0	151.6

sequent decomposition and on completion of the $\gamma\text{-}Al_2O_3 \rightarrow$ $\alpha\text{-}Al_2O_3$ transition.

The firing conditions selected on the basis of the kinetic studies make it possible to obtain high-alumina wear-resistant ceramics with a fine-crystalline structure, a compressive strength of $1750 - 1800$ MPa, and a bending strength of $600 - 700$ MPa.

Thus, use of the structure/energy parameter n as a dependent variable to characterize the process of material compaction in sintering significantly simplifies the mathematical description of the compaction kinetics compared to the use of other variables, and the existence of kinetic regularities is the basis for the interpretation of the compaction mechanism and the selection of the ceramic firing conditions.

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